

AD-A235 264

INTATION PAGE

Form Approved
OMB No. 0704-0188

Read to average 1 hour per review, including the time for reviewing instructions, searching existing data sources, reviewing the collection of information, sending comments regarding the burden estimate or any other aspect of this burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Report
4. TITLE AND SUBTITLE Structural Transformations in Crystalline Oligomers of Polyparaphenylene			5. FUNDING NUMBERS 61102F 2303/A3
6. AUTHOR(S) Kenneth N. Baker, Howard C. Knachel, Albert V. Fratini, and w. Wade Adams.			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Dayton 300 College Park Dayton, OH 45469-0001			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-91 0470
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Building 410, Bolling AFB, DC 20332-6448			10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFOSR-88-0044
11. SUPPLEMENTARY NOTES Mat. Res. Soc. Symp. Proc. Vol. 134, 1989 Materials Research Society, pg 497-503			
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION STATEMENT DTIC ELECTIC MAY 07 1991 S 6
13. ABSTRACT (Maximum 200 words) <p>We report the room and low temperature crystal structures of the unsubstituted p-quinquephenyl (PQP) and p-sexiphenyl (PSP), and substituted 2,2',4,4'-diphenyl-p-quinquephenyl (DPQP), 2,2',6,6'-diphenyl-p-sepuphenyl (DPSP), and 1,2,4-triphenylbenzene (TPB) polyparaphenylene oligomers. The unsubstituted oligomers exhibit a solid state transition when cooled from room temperature to 110K, as indicated by a change in crystallographic space group. No transition is observed for the substituted oligomers other than the usual thermal contraction of the unit cell. The transition observed for the unsubstituted oligomers is interpreted in terms of a conformational change from an "averaged" planar structure to a static non-planar one. Comparisons of room temperature and low temperature crystal data are presented.</p>			
14. SUBJECT TERMS			
15. NUMBER OF PAGES			
16. PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT

DTIC FILE COPY

STRUCTURAL TRANSFORMATIONS IN CRYSTALLINE OLIGOMERS OF POLYPARAPHENYLENE

KENNETH N. BAKER*, HOWARD C. KNACHEL*, ALBERT V. FRATINI*, and W. WADE ADAMS**

*Department of Chemistry, University of Dayton, 300 College Park, Dayton, OH 45469.

**Materials Laboratory, Wright Research and Development Center, WPAFB, OH 45433-6533.

ABSTRACT

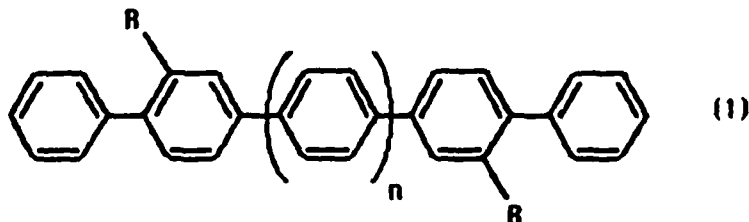
We report the room and low temperature crystal structures of the unsubstituted p-quinquephenyl (PQP) and p-sexiphenyl (PSP), and substituted 2,2',4,4'-diphenyl-p-quinquephenyl (DPQP), 2,2',6,6'-diphenyl-p-septiphenyl (DPSP), and 1,2,4-triphenylbenzene (TPB) polyparaphenylene oligomers. The unsubstituted oligomers exhibit a solid state transition when cooled from room temperature to 110K, as indicated by a change in crystallographic space group. No transition is observed for the substituted oligomers other than the usual thermal contraction of the unit cell. The transition observed for the unsubstituted oligomers is interpreted in terms of a conformational change from an "averaged" planar structure to a static non-planar one. Comparisons of room temperature and low temperature crystal data are presented.

INTRODUCTION

Oligomers of polyparaphenylene (PPP) have been of interest in our laboratory as part of continuing research on the structure and morphology of rigid-rod polymers. Aerospace applications requiring a broad range of operating temperatures and conditions require that any structural transition temperatures must be known. Much basic morphological information is still needed about factors such as the orientation of one coaxial ring to another and crystal packing forces in high performance polymers of this type.

Tedious synthetic procedures coupled with a high melting point and low solubility have made PPP a difficult polymer to prepare and fabricate[1,2]. P-polyphenyls with a specific chain length and incorporating pendant groups have been recently prepared using a new synthesis procedure utilizing intermolecular cyclization[3].

We have obtained high purity samples of PPP oligomers from which single crystals of sufficient size for structure analysis were sublimed or recrystallized. In a continuing investigation of the molecular structure, crystal packing, and structural transformations of PPP oligomers, we have studied p-quinquephenyl (PQP), p-sexiphenyl (PSP), 2,2',4,4'-diphenyl-p-quinquephenyl (DPQP), 2,2',6,6'-diphenyl-p-septiphenyl (DPSP), and 1,2,4-triphenylbenzene (TPB). The first four compounds have the general structure (1)



where $n = 1$ and $R = H$ for PQP, $n = 1$ and $R = \text{phenyl}$ for DPQP, $n = 2$ and $R = H$ for PSP, and $n = 3$ and $R = \text{phenyl}$ for DPSP. TPB was included in this present study since its room temperature structure has not been reported.

EXPERIMENTAL METHODS

Samples of PQP, PSP, DPQP, DPSP, and TPB were obtained from Bruce Reinhardt, Materials Laboratory, Wright Patterson Air Force Base. PQP and PSP samples were sublimed to obtain good quality crystals; otherwise, the samples needed no additional purification. Data were collected on an Enraf Nonius CAD4 diffractometer interfaced to a Digital Equipment Corporation Micro PDP-11 computer. Data refinement and structure determination were accomplished using the Structure Determination Package (SDP)[4] software on a Digital Equipment Corporation VAX 11/730 computer. The final R values and the corresponding ratio of the number of unique reflections to the number of parameters varied are 0.050 (663:136), 0.062 (623:163), 0.049 (1061:190), 0.046 (1537:244), and 0.036 (1839:219) for PQP, PSP, DPQP, DPSP, and TPB, respectively. Complete structural information will be given in another publication[15]. Cooling of the crystal was accomplished with an Enraf Nonius FR558NH liquid nitrogen cryostat for the CAD4 instrument.

RESULTS AND CONCLUSIONS

Table I summarizes current results along with published results for biphenyl(BP), p-terphenyl(PTP), and p-quaterphenyl(PQuatP) and one can see several trends. As the number of phenyl units in the oligomer chain increases, one observes a direct increase of approximately 4.1 Å in the c lattice dimension of the monoclinic unit cell per paraphenylene unit. This distance is slightly less than the length of a phenylene unit so one would expect the oligomer axis to be approximately aligned with the c crystallographic axis. The unit cell diagrams included in Figure 1 confirm that the oligomer axis is preferentially aligned with the c crystallographic axis.

The low temperature unit cell is a superlattice of the room temperature unit cell with parameters a and b doubled to account for the greater displacement of the non-planar oligomer. The low temperature crystal structures of PTP[8] and PQuatP[10] were solved using a triclinic unit cell. At room temperature the crystal structure indicates a planar oligomer probably resulting from the average of several non-planar conformations. At low temperature a specific non-planar geometry is preferred.

Figure 2 summarizes the melting points of p-polyphenyls and their respective transition temperatures. A steady rise in temperature is observed as the oligomer increases in length so that the predicted transition temperatures for PQP and PSP should be above room temperature. However we report here that the structures of PQP and PSP remain planar at room temperature and Differential Scanning Calorimetry (DSC) measurements indicate that there is no transition other than melting at higher temperatures. Upon cooling of PQP and PSP single crystals to 110K, unit cells very similar to the room temperature unit cells were found initially. However, after 24 hours a crystal phase transition had occurred. Both DSC analysis and X-ray powder diffraction patterns taken as low as 143K and held for several days revealed no structural transition. We conclude that the transition temperature must exist between 143K and 110K, as indicated by the error bars in Figure 2, and is time dependent. This transition could be non-first order as observed for biphenyl[5,6] in which a soft mode exists below its transition temperature. More experiments are planned to study this phenomenon.

As is the case for most high temperature-resistant polymers, PPP degrades before it melts; however, for comparison purposes there is interest in knowing the theoretical melting point of the polymer. Literature reports PPP to be infusible[11], but by the extrapolation of experimental melting points of PPP oligomers (Figure 3) we estimate the melting point of PPP to be 1020K. Extrapolated melting points of 620K and 1260K have been reported for poly(tetrafluoroethylene)[12] and KevlarTM[13], respectively. Those extrapolations are based on melting point depression associated with end group concentration in polymers[14].

The low temperature crystal structure of DPQP is isostructural with its room temperature crystal structure indicating no structural transition. In a paper to be published elsewhere[15] we report that the addition of pendant groups to the PPP oligomer results in a distortion of planarity of the unsubstituted oligomer, but the torsion angles change less than an average of

TABLE I

VARIABLE TEMPERATURE CRYSTAL DATA

Compound	Temperature(K)	Space Group	a(Å)	b(Å)	c(Å)	alpha(°)	beta(°)	gamma(°)
BP	298[5]	P2 ₁ /c*	9.51(2)	5.63(1)	8.12(2)	90	95.1(3)	90
BP	40[6]	P2 ₁ /c*	9.51(2)	11.26(2)	16.24(4)	90	95.1(3)	90
PTP	298[7]	P2 ₁ /c*	13.613(6)	5.613(2)	8.106(4)	90	92.2(2)	90
PTP	191[7]	P2 ₁ /c*	13.53(3)	11.09(3)	16.01(3)	90	92.0(2)	90
PQualP	298[9]	P2 ₁ /c*	17.910(10)	5.610(4)	8.110(6)	90	95.80(6)	90
PQualP	243[10]	P2 ₁ /c*	17.70(3)	11.16(2)	15.97(3)	90	95.61(8)	90
PQP	298	P2 ₁ /c	22.056(4)	5.581(1)	8.070(1)	90	97.91(1)	90
PQP	110	monoclinic, C centered	22.014(3)	11.029(4)	15.968(6)	90	98.18(2)	90
PSP	298	P2 ₁ /c	26.241(5)	5.568(1)	8.091(3)	90	98.17(2)	90
PSP	110	monoclinic, C centered	26.282(8)	10.999(4)	15.995(9)	90	99.79(4)	90
PSeplP	298	P2 ₁ /c*	30.232(19)	5.574(3)	8.065(5)	90	94.85(5)	90
PSeplP	110	work in progress						
DPQP	298	P2 ₁ /c	6.304(3)	31.437(9)	7.651(3)	90	106.18(4)	90
DPQP	110	P2 ₁ /c	6.265(2)	31.345(9)	7.510(2)	90	106.08(2)	90
DPSP	298	P1	11.713(2)	13.596(2)	6.138(2)	102.33(2)	96.51(2)	102.71(1)
DPSP	110	work in progress						
TPB	298	Pbca	10.368(6)	17.898(4)	18.474(5)	90	90	90
TPB	110	work in progress						

* For comparison purposes, the P2₁/a space groups were transformed to P2₁/c.

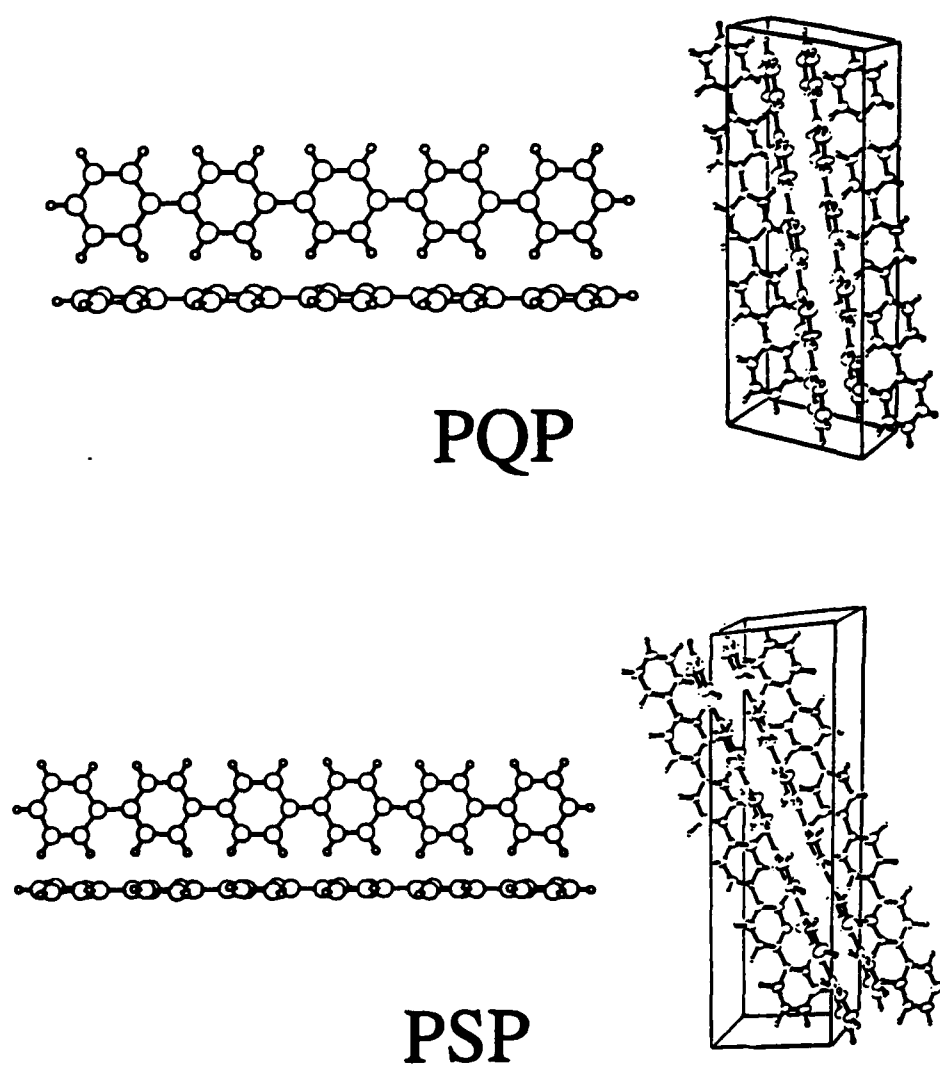


Figure 1. Flat, side and unit cell views of PQQ and PSP.

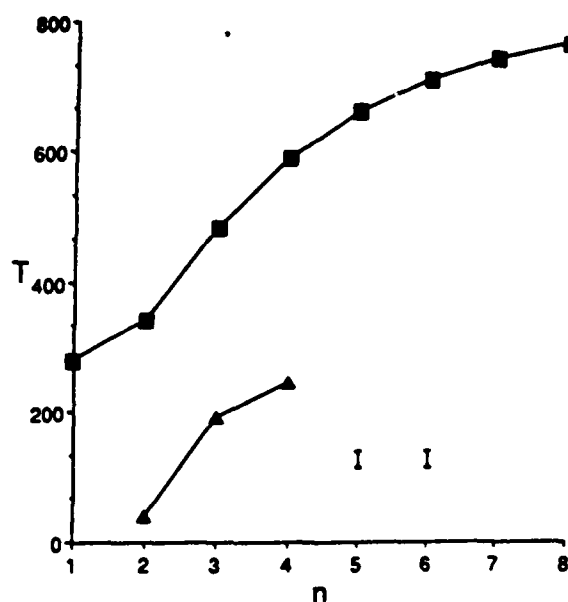


Figure 2. Plot of transition (\triangle , K) and melting point (\square , K) vs. oligomer length (n). Melting point data, taken from DSC measurements, are as follows: 279K[2], 343K[2], 483K[2], 591K[2], 661K[3], 710K[3], 741K[3], and 764K[3] for $n = 1 - 8$, respectively. Transition temperatures are 40K[6], 191K[7], and 243K[10] for $n = 2 - 4$, respectively. Error bars at $n = 5$ and 6 indicate temperature range for observed transition.

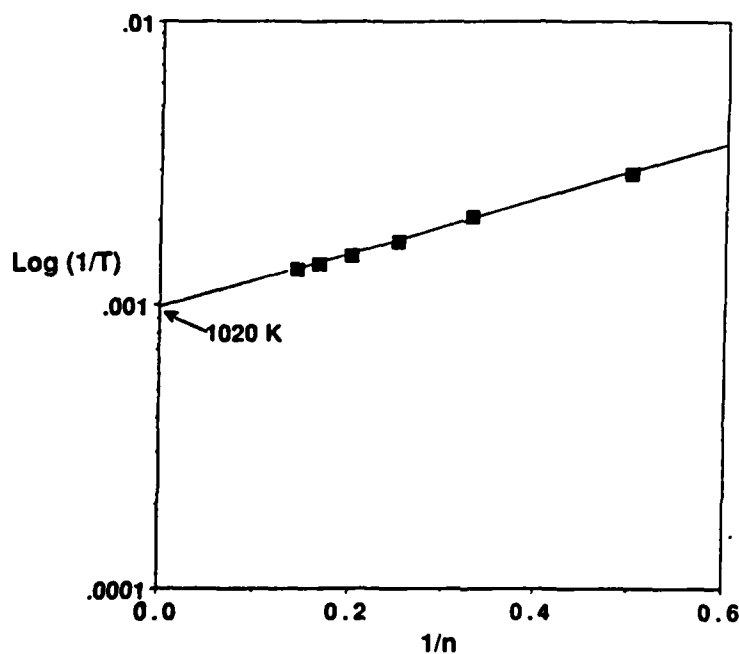


Figure 3. Plot of log of inverse melting point ($\log(1/T)$, K) vs. inverse oligomer length ($1/n$) showing the extrapolated melting point of high polymer PPP.

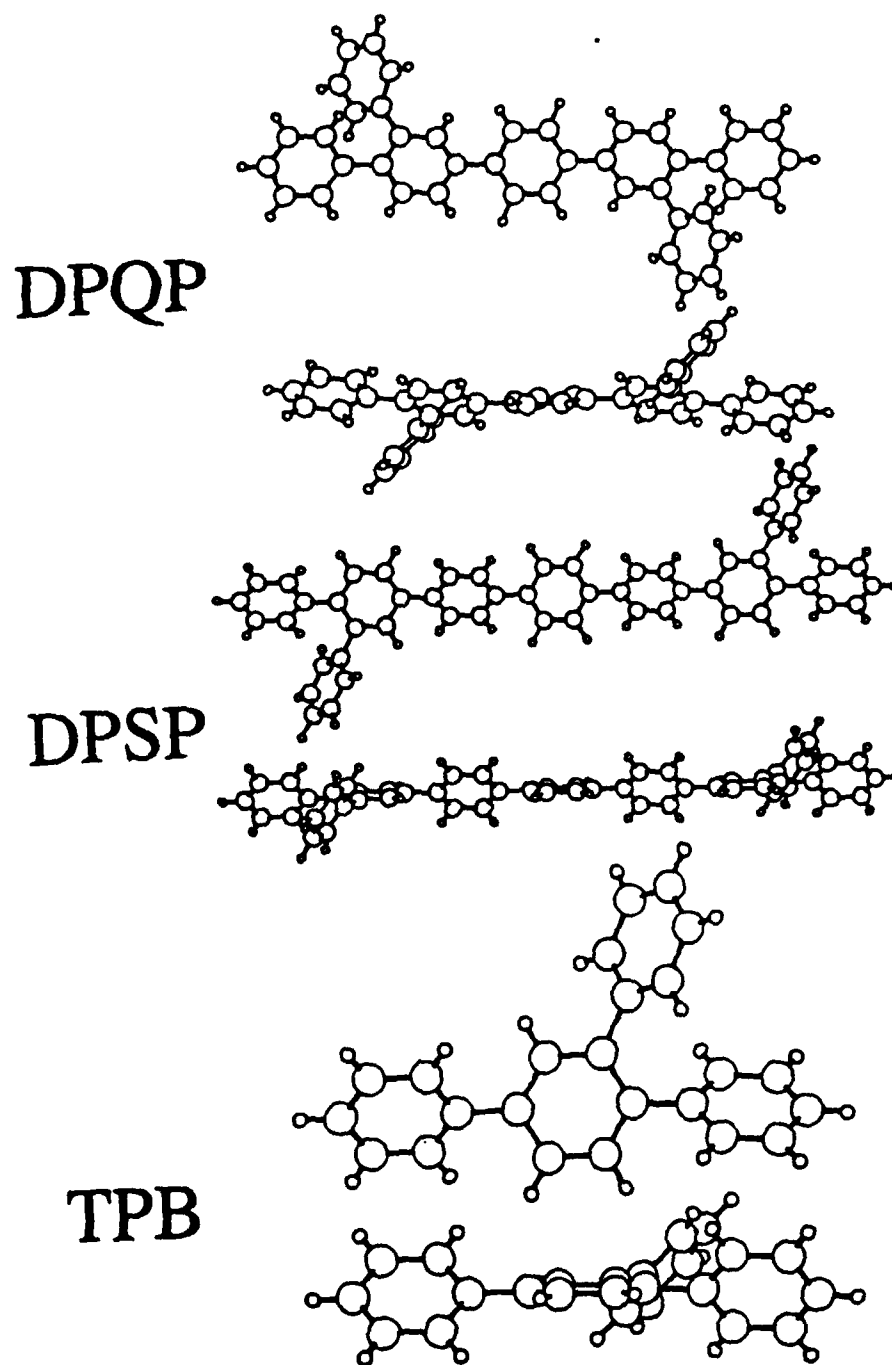


Figure 4. Molecular views of DPQP, DPSP and TPB.

10° between room and low temperature. As the length of the substituted PPP oligomer increases, a systematic decrease in symmetry is observed as a change in space group. The substituted oligomers are presented in Figure 4 and the molecules form a herringbone pattern in the unit cell. More compounds in this series are being studied.

Molecular modeling studies of PPP oligomers are complementing structure investigations. The calculated torsion angle for biphenyl is approximately twice that calculated for the rigid-rods poly(p-phenylenebenzobisthiazole) (PBZT) and poly(p-phenylenebenzobisoxazole) (PBO)[16,17]. The torsion angles calculated for a phenyl substituted biphenyl molecule in its lowest energy conformation agree with crystallographic data for substituted PPP oligomers. PPP conformations simulated in the absence of crystal packing forces have the rings perpendicular to each other. This suggests that the constraints within the unit cell are strong enough to overcome the ortho-hydrogen repulsion. Recent calculations show PPP to have a high theoretical axial tensile modulus and a high compressive strength, which encourages continued interest in PPP oligomers as potential structural materials[17].

REFERENCES

1. G.K. Noren and J.K. Stille, *J. Polym. Sci. Macromol. Rev.* **5**, 385 (1971).
2. J.G. Speight, P. Kovacic, and F.W. Koch, *J. Macromol. Sci. Rev. Macromol. Chem.* **5**, 295 (1971).
3. M.R. Unroe and B.A. Reinhardt, *Polymer* **11**, 981 (1987).
4. B.A. Frenz and Associates, Inc. (1985), College Station, Texas, 77840.
5. A. Bree and M. Edelson, *Chem. Phys. Lett.* **46** (3), 500 (1977).
6. H. Cailleau, J.L. Baudour, and C.M.E. Zeyen, *Acta Cryst.* **B35**, 426 (1979).
7. H. Cailleau and A. Dworkin, *Mol. Cryst. Liq. Cryst.* **50**, 217 (1979).
8. J.L. Baudour, Y. Delugeard, and H. Cailleau, *Acta Cryst.* **B32**, 150 (1976).
9. B.A. Bolton and P.N. Prasad, *Chem. Phys.* **35**, 331 (1978).
10. J.L. Baudour, Y. Delugeard, and P. Rivet, *Acta Cryst.* **B34**, 625 (1978).
11. P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.* **85**, 454 (1963).
12. H.W. Starkweather, *Macromolecules* **19**, 1131 (1986).
13. K. Gardner (Private Communication).
14. P.J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953) p. 570.
15. K.N. Baker, H.C. Knachel, A.V. Fratini, and W.W. Adams, to be published.
16. B.L. Farmer (Private Communication).
17. S.G. Wierschke, *AFWAL-TR-88-4201* (October 1988).